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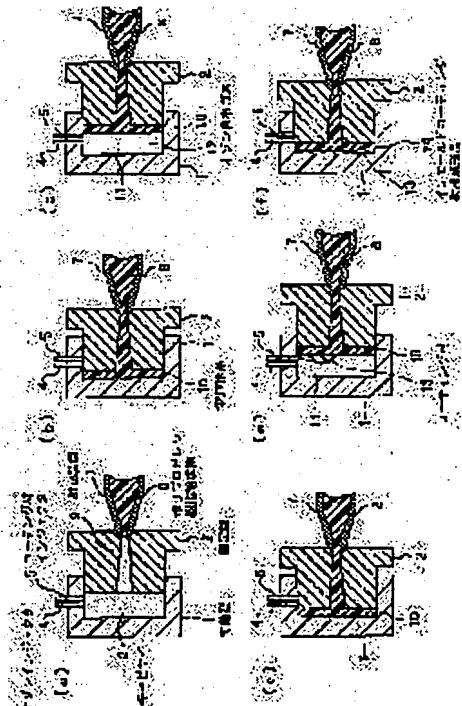
(72)Inventor : AKIMOTO HIDEO

(54) MANUFACTURING METHOD FOR IN-MOLD COATING INJECTION- MOLDED ARTICLE, AND INJECTION-MOLDED ARTICLE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a manufacturing method for an in-mold coating injection- molded article wherein a coating layer being excellent in adhesion can be efficiently formed in molding dies simultaneously with the injection-molding, even for injection-molded articles with a polyolefin resin having no functional group as the major material, and in addition, an injection-molded article having a favorable appearance can be obtained.

SOLUTION: A polypropylene resin composition 8 which is molten by an injection device 7 is injected and filled in a cavity 3. Then, the polypropylene resin composition 8 is cooled and solidified, and a primary molded article 10 is obtained (b). Then, a secondary space 11 is formed between the primary molded article 10 and a movable die 1, and a gas 12 containing ozone is injected from an ozone injector 4. Thus, ozone in the gas 12 containing ozone is brought into contact with the primary molded article 10 (c). After discharging the gas 12 containing ozone (d), a coating material 13 is injected (e) into the secondary space 11 from a coating material injector 5, and the coating material 13 is hardened (f).



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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the manufacture approach of the manufacture approach of the in mould coating injection-molded product which uses polyolefin resin as the main raw material and an injection-molded product, especially the in mould coating injection-molded product that uses polypropylene resin as the main raw material, and an injection-molded product.

[0002]

[Description of the Prior Art] Polyolefin resin is used widely industrially. Especially, excluding chlorine, even if it destroys by fire, harmful gas does not occur, and since recycle is also possible, polyolefin resin is used focusing on the automobile or the building material application as an environment-friendly ingredient.

[0003] The thing which generally carried out coating (paint) of the components which consist of polyolefin resin used for an automotive application since importance was attached to an appearance, or the layered product which stretched epidermis material is used. However, the coating process which uses a solvent for a large quantity from an environmental problem in recent years can be skipped, or the lamination of epidermis material can be omitted, and the mold goods with which an appearance moreover consists of good polyolefin resin are demanded.

[0004] as one of the techniques which can cope with such [recently] an environmental problem, the approach (it may be hereafter called in mould coating) of coating resin mold goods with a coating material in a mold within shaping of resin, simultaneously shaping metal mold is proposed to synthetic-resin components (for example, JP,8-332655,A).

[0005] However, in the conventional in mould coating shaping approach, when polyolefin resin is used as a raw material of mold goods, since polyolefin resin does not have a functional group, even if it is inferior to an adhesive property with the coating material which carries out in mould coating and it coats it with much trouble for this reason, it has the trouble that a coating material may exfoliate and lose touch with polyolefin resin mold goods with heating cooling at the time of practical use, or stress.

[0006]

[Problem(s) to be Solved by the Invention] The technical problem of this invention is offering the manufacture approach of an in mould coating injection-molded product and injection-molded product which can form the coating layer excellent in the adhesive property in injection molding and coincidence efficiently within shaping metal mold also to the injection-molded product which uses as the main raw material the polyolefin resin which does not have a functional group, and can moreover obtain an injection-molded product with a good appearance.

[0007]

[Means for Solving the Problem] This inventions are the manufacture approach of the following in mould coating injection-molded product, and an injection-molded product.

- (1) In the manufacture approach of an in mould coating injection-molded product of coating the injection-molded product which uses polyolefin resin as the main raw material within metal mold, and

manufacturing an in mould coating injection-molded product. The primary forming cycle which injects the raw material which uses as a principal component the polyolefin resin which carried out heating fusion to the cavity formed from a male and a female mold, and fabricates primary mold goods. The ozone contact process of making a male and a female mold estranging, forming space between metal mold and primary mold goods, supplying ozone content gas to this space, and making the front face of primary mold goods contacting. The manufacture approach of the in mould coating injection-molded product which includes the coating process which stiffens a coating material after pouring a coating material into the space formed between the exhaust gas process which discharges ozone content gas from metal mold, and metal mold and primary mold goods and coating primary mold goods.

(2) The manufacture approach of the above-mentioned (1) publication that polyolefin resin is polypropylene resin.

(3) The in mould coating injection-molded product manufactured from the manufacture approach the above (1) or given in (2).

[0008] By the manufacture approach of the in mould coating injection-molded product of this invention, the raw material which uses polyolefin resin as a principal component as a raw material of mold goods is used. As this raw material, only polyolefin resin can also be used, the polyolefin resin constituent with which other resin, rubber, additives, etc. were blended can also be used, and that which can injection mold can use it without a limit.

[0009] The polyolefin resin used by this invention is the homopolymer or copolymer which uses an alpha olefin as the main monomer components, and if it is resin which can injection mold, it can be especially used without a limit. as the above-mentioned alpha olefin -- the carbon numbers 2-20, such as ethylene, a propylene, 1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, 1-dodecen, 1-tetra-decene, 1-hexa-decene, and 1-octadecene, -- the alpha olefin of 2-10 is raised preferably. These alpha olefins can also be used by the one-sort independent, and can also be used combining two or more sorts.

[0010] As a concrete thing of the polyolefin resin used by this invention, well-known polyethylene resin, polypropylene resin, polybutene -1, poly4 methyl 1 pentene, an ethylene-vinylacetate copolymer, an ethylene acrylic ester copolymer, an ethylene methacrylic ester copolymer, an ionomer, etc. are raised. In these, a viewpoint to the polyethylene resin and polypropylene resin of cost performance, a mechanical strength, and a moldability are desirable, and especially polypropylene resin is desirable.

[0011] As polyethylene resin, either high density polyethylene medium density polyethylene or low consistency poly ECHIRE can be used preferably. Polyethylene resin can use preferably either the homopolymer of ethylene a random copolymer or a block copolymer.

[0012] As polypropylene resin, the homopolymer of a propylene, a copolymer with the alpha olefin of carbon numbers 2-10 other than a propylene and a propylene, etc. are raised. In the case of a copolymer, it has a desirable comonomer content less than [10 mol %] and that it is less than [5 mol %] preferably. As a comonomer, ethylene, 1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, etc. are raised. In these, ethylene is desirable. Polypropylene resin can use preferably either a homopolymer a random copolymer or a block copolymer.

[0013] Foaming can also be performed adjusting the crystallization rate at the time of foaming also being able to use polypropylene resin by the one-sort independent, also being able to use it combining two or more sorts, considering as the compound suitably combined out of the homopolymer, the random copolymer, and the block copolymer according to the application and thickness of mold goods, and holding the target mechanical strength. When high crystallinity polypropylene resin is used especially, combination of a random copolymer can adjust a crystallization rate.

[0014] Polyolefin resin, such as polypropylene resin used by this invention, can be manufactured by the well-known approach. For example, it can manufacture by carrying out the polymerization of the monomer to the bottom of existence of the catalyst system which consists of the solid-state catalyst component (a), the organic aluminium (b), and the electron donor (c) containing magnesium, titanium, a halogen, and an electron donor.

[0015] An olefin system elastomer can be blended with the raw material of the mold goods used by this

invention in the range which does not spoil the object of this invention. The elastic copolymer of amorphism which consists of carbon numbers 2-20 and a copolymer which makes the alpha olefin of 2-10 the main monomer preferably as an olefin system elastomer can use it without a limit. As a concrete thing of an alpha olefin, ethylene, a propylene, 1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, 1-dodecen, 1-tetra-decene, 1-hexa-decene, 1-octadecene, etc. are raised. These alpha olefins can also be used by kind independent, and can also use two or more sorts together.

[0016] As a concrete thing of an olefin system elastomer, ethylene and alpha olefin copolymers, such as ethylene propylene rubber, an ethylene butene copolymer, an ethylene hexene copolymer, an ethylene octene copolymer, and an ethylene decene copolymer, a propylene butene copolymer, a propylene butene ethylene copolymer, etc. are raised.

[0017] An olefin system elastomer can also be used by the one-sort independent, and can also be used combining two or more sorts. By blending an olefin system elastomer, mold goods excellent in shock resistance are obtained.

[0018] An olefin system elastomer can be obtained by the well-known approach, and can usually copolymerize and obtain a monomer under a gaseous phase or the liquid phase under existence of a transition metal catalyst. There is especially no constraint in the catalyst and polymerization method for manufacture, for example, a Ziegler type catalyst, the Philips mold catalyst, a metallocene mold catalyst, etc. can be used, and a polymerization can be carried out with polymerization methods, such as a gaseous-phase method, a solution method, and a bulk polymerization method.

[0019] An inorganic bulking agent can be blended with the raw material of the mold goods used by this invention in the range which does not spoil the object of this invention. An inorganic bulking agent well-known as an inorganic bulking agent can use it without a limit, for example, talc, a silica, a mica, a calcium carbonate, a glass fiber, a glass bead, a barium sulfate, a magnesium hydroxide, a WARASU night, calcium silicate fiber, a carbon fiber, magnesium oxy-sulfate fiber, a potassium titanate fiber, titanium oxide, calcium sulfite, white carbon, clay, a calcium sulfate, etc. are raised. An inorganic bulking agent can also be used by the one-sort independent, and can also be used combining two or more sorts. By blending an inorganic bulking agent, rigidity is high and mold goods excellent in dimensional accuracy are obtained.

[0020] the range which does not spoil the object of this invention in the raw material of the mold goods used by this invention -- resin [other than polyolefin resin]; -- rubber-like polymers, such as copolymer rubber other than said olefin system elastomer and conjugated diene rubber, etc. can be blended suitably. Moreover, various additives can also be added if needed. As an additive, well-known additives, such as flow nature amelioration agents, such as a nucleating additive, an antioxidant, a hydrochloric-acid absorbent, a heat-resistant stabilizer, a weathering stabilizer, light stabilizer, an ultraviolet ray absorbent, a slipping agent, an anti blocking agent, an antifogger, lubricant, an antistatic agent, a flame retarder, a pigment, a color, a dispersant, copper inhibitor, a neutralizer, a foaming agent, a plasticizer, a cellular inhibitor, a cross linking agent, and a peroxide, a weld on-the-strength amelioration agent, natural oil, synthetic oil, and a wax, be raised.

[0021] Said olefin system elastomer blended with the raw material of mold goods, an inorganic bulking agent, resin, a rubber-like polymer, and various additives can also be blended independently, and it can combine and they can also be blended with arbitration.

[0022] The raw material, i.e., the polyolefin resin, or the polyolefin resin constituent especially the polypropylene resin, or the polypropylene resin constituent of the mold goods used by this invention is ASTM. D 1-200g / that they are 2-150g / 10min preferably have the desirable melt flow rate (MFR) measured by 1238 under 230 degrees C and 2.16kg load 10 min. When MFR is in the above-mentioned range, high-speed injection is possible, and also it is easy to adjust the balance of rigidity and shock resistance.

[0023] A well-known coating material (coating) can be used for the coating material used by this invention, and it is not restricted especially. For example, the 2 liquid type coating material which mixes base resin/curing agent is raised just before metal mold impregnation of the 1 liquid type coating

material which makes a subject the binder component which can be hardened by peroxide cross linking agents, such as polyfunctional acrylate resin, polyfunctional methacrylate resin, an unsaturated polyester resin, epoxy acrylate oligomer, and urethane acrylate oligomer, an epoxy resin / polyamine hardening system, polyol resin / poly isocyanate hardening system, etc., etc.

[0024] While carrying out melting kneading, injection molding said raw material using the injection-molding equipment which has the following property and manufacturing an injection-molded product, it coats with this invention within metal mold. The injection-molding equipment and metal mold which are used with this shaping possess the following property.

- 1) The content volume of a cavity is changeable.
- 2) Ozone content gas can be introduced in a cavity, and it can discharge.
- 3) A coating material can be poured in in a cavity.

[0025] Although ozone gas can also be used as ozone content gas used by this invention, it is desirable to use the ozone content gas by which ozone gas is diluted by the carrier gas of ozone, such as air, nitrogen, carbon dioxide gas, and oxygen. As for the concentration of the ozone in ozone content gas, it is usually preferably desirable that it is 1 - 200 g/m³ about three 0.5 - 300 g/m.

[0026] Ozone content gas can be obtained using a well-known ozone generator. The equipment which electrolyzes the moisture in (i) air, for example, and obtains ozone as an ozone generator, the equipment which carries out electrodisscharge treatment of the oxygen in (ii) air, and obtains ozone, the equipment which carries out electrodisscharge treatment of the pure (iii) oxygen, and obtains ozone can be used.

[0027] In the manufacture approach of this invention, the raw material of said mold goods which carried out heating fusion is injected in a cavity, and primary mold goods are fabricated by the primary forming cycle. This injection molding can be performed by the same approach as the conventional injection molding.

[0028] At an ozone contact process, move a male and/or a female mold, a male and a female mold are made to estrange relatively, and this forms space between metal mold and primary mold goods. And ozone content gas is supplied to this space, and ozone and primary mold goods are contacted. Migration (formation of space) of metal mold can also be performed supplying ozone content gas (impregnation). As for the contact time of ozone and primary mold goods, it is preferably desirable for 1 - 300 seconds that it is for 10 - 100 seconds.

[0029] The front face of primary mold goods oxidizes by ozone, and is activated by such ozone contact processing. For this reason, even if it uses the polyolefin resin which does not have a functional group as a raw material of mold goods, the adhesive property of mold goods and a coating material can improve, and the coating layer (paint film) excellent in the adhesive property (adhesion) can be made to form.

[0030] At an exhaust gas process, it permutes with air, or decompresses, or an ejector half is moved, and the ozone content gas used at the ozone contact process is discharged from metal mold by the approach of reducing cavity path clearance. The discharged ozone content gas can be processed by the usual art.

[0031] At a coating process, said coating material is poured into the space formed between metal mold and primary mold goods, after extending and coating homogeneity on the front face of primary mold goods, coating-material hardening is carried out and a coating layer is formed. When the space which pours in a coating material between metal mold and primary mold goods after said exhaust gas process termination is not secured enough (for example, when the ejector half was moved, cavity path clearance was reduced and ozone content gas is discharged), a coating material is poured in, after moving metal mold and securing space required for impregnation of a coating material. The injection-molded product to which coating which was excellent in the adhesive property on the surface of mold goods was performed according to the coating process is obtained. As for the thickness of a coating layer, it is preferably desirable that it is 10 micrometers - 100 micrometers still more preferably 10 micrometers - 1mm 1 micrometer - 3mm.

[0032] Thus, the polyolefin resin layer whose in mould coating injection-molded products obtained are a coating layer and a base material is excellent in the adhesive property, and a cold energy cycle trial cannot exfoliate easily, either. And since a metal mold inner surface is imprinted by the coating layer good compared with paint metal mold outside, a paint film with good mirror plane and crimp side is

formed, and mold goods excellent in the appearance are obtained.

[0033] The in mould coating injection-molded product of this invention is an in mould coating injection-molded product obtained by the manufacture approach of said in mould coating injection-molded product.

[0034] The in mould coating injection-molded product of this invention can be used in various fields, such as housing for automobile exterior-parts; household electric appliances, such as automobile interior part; side protection malls, such as a door trim and an instrument panel, a bumper, software FEISHA, and a mud guard, office supplies, a general cargo for days, kitchen utensils, a building-materials supply, and sporting goods.

[0035]

[Effect of the Invention] Since the manufacture approach of the in mould coating injection-molded product of this invention pours a coating material into metal mold and forms the coating layer after it contacts ozone content gas and an injection-molded product within metal mold, it can make the coating layer excellent in the adhesive property able to form in injection molding and coincidence within shaping metal mold to the injection-molded product which uses as the main raw material the polyolefin resin which does not have a functional group, and, moreover, can manufacture an injection-molded product with a good appearance efficiently. Since the in mould coating injection-molded product of this invention is an in mould coating injection-molded product obtained from the above-mentioned manufacture approach, the coating layer excellent in the adhesive property is making it form to the injection-molded product which uses as the main raw material the polyolefin resin which does not have a functional group, and, moreover, its appearance is good.

[0036]

[Embodiment of the Invention] Hereafter, an example of the manufacture approach of this invention is explained using a drawing. Drawing 1 is process transition drawing showing an example of the manufacture approach of the in mould coating injection-molded product of this invention, and is illustrated as the typical vertical cross section of metal mold and equipment. (a) of drawing 1 -- before injection initiation of a polypropylene resin constituent, in ozone content gas-charging termination and (d), ozone content gas blowdown termination and (e) show coating-material impregnation, and, as for (b), (f) shows [injection termination and (c)] the event of coating-material hardening. A production process changes in order of (a), (b), (c), (d), (e), and (f).

[0037] In drawing 1 , 1 is the ejector half of a female mold, 2 is the cover half of a male, and these constitute the injection molding die. An ejector half 1 can be moved to a longitudinal direction to a cover half 2, and it is constituted so that an ejector half 1 may be pressed to a cover half 2 and a cavity 3 may be formed in the interior of metal mold. Moreover, metal mold has the so-called share edge structure where the polypropylene resin constituent with which it filled up even if it changed the cavity volume does not leak.

[0038] The coating-material injector 5 which injects into a cavity 3 the ozone injector 4 and coating material which supply ozone content gas to a cavity 3 is formed in the ejector half 1. The ozone injector 4 is connected to the ozone generator installed in the metal mold exterior through the conduit which has osone-proof nature, such as corrosion resistance metal or Teflon (trademark), and although it is constituted so that ozone content gas can be supplied to a cavity 3, the graphic display of a conduit and an ozone generator is omitted.

[0039] Moreover, the coating-material injector 5 is connected to the coating-material regurgitation pump installed in the metal mold exterior through the flexible tube, and although the coating material stored in the coating-material tank is constituted so that a regurgitation pump may be driven and can be injected into a cavity 3, the graphic display of a flexible tube, a coating-material regurgitation pump, and a coating-material tank is omitted. The polypropylene resin constituent with which 7 becomes injection equipment and 8 becomes the raw material of mold goods, and 9 are sprues.

[0040] In order to manufacture an in mould coating injection-molded product with the equipment of drawing 1 , an ejector half 1 is first advanced from the condition of (a) of drawing 1 , and metal mold is closed. Next, injection restoration of the polypropylene resin constituent 8 fused with injection

equipment 7 is carried out into a cavity 3 from sprue 9, it cools and solidifies after that, and the primary mold goods 10 are obtained ((b) of drawing 1, primary forming cycle).

[0041] As for the resin temperature of the polypropylene resin constituent 8 to inject, it is preferably desirable that it is 180-260 degrees C 170-270 degrees C. Moreover, as for die internal pressure, it is preferably desirable that it is 10-15MPa five to 20 MPa.

[0042] Next, move an ejector half 1, the primary mold goods 10 and an ejector half 1 are made to estrange, and the secondary space 11 is formed between the primary mold goods 10 and an ejector half 1. this secondary space 11 -- an ozone level -- 0.5-300g/m³ -- the ozone content gas 12 of 1 - 200 g/m³ is preferably poured in from the ozone injector 4, and the ozone and the primary mold goods 10 in ozone content gas 12 are contacted ((c) of drawing 1, ozone contact process). When impregnation of this ozone content gas 12 is performed to migration actuation and coincidence of an ejector half 1, since die opening actuation can be performed smoothly, it is desirable. The injection rate to the secondary space 11 of ozone content gas 12 is an amount corresponding to the volume of the secondary space 11. For example, what is necessary is just to carry out 2 liter extent supply, when projected area is [the travel of an ejector half 1] 2mm in the mold goods of 2 1m.

[0043] As for the contact time of ozone content gas 12 and the primary mold goods 10, it is preferably desirable for 1 - 300 seconds that it is for 10 - 100 seconds. The front face of the primary mold goods 10 exposed to ozone content gas 12 according to this ozone contact process is activated by oxidation reaction, and the outstanding adhesive property with the coating material by which coating is carried out at the following process is given.

[0044] Ozone content gas 12 is discharged by moving an ejector half 1 and reducing cavity path clearance after the above-mentioned contact time progress through the exhaust hole (not shown) in which it was prepared by the share edge section ((d) of drawing 1, exhaust gas process). What is necessary is just to process the discharged ozone content gas 12 by the usual art.

[0045] An ejector half 1 is moved and the secondary space 11 is formed. Thickness a coating material 13 from the coating-material injector 5 to this secondary space 11 Next, 1 micrometer - 3mm, After pouring in so that it may be set to 10 micrometers - 100 micrometers still more preferably ((e) of drawing 1, coating process), advancing an ejector half 1 and opening a mold clamp meal and a coating material 13 to homogeneity, it is made to harden 10 micrometers - 1mm preferably ((f) of drawing 1, coating process). Thereby, the in mould coating injection-molded product 14 with which coating of the coating material 13 was carried out to the front face of the primary mold goods 10 can be obtained.

[0046] After setting early die path clearance to 1.0mm, more specifically injecting some polypropylene resin constituents 8 to a cavity 3 and fabricating the primary mold goods 10, ozone content gas 12 is supplied to the secondary space 11, retreating die path clearance to 2.0mm. It is left in the condition for 20 seconds, and while advancing an ejector half 1 1.9mm subsequently, ozone content gas 12 is discharged. Next, thermosetting acrylics is supplied from the coating-material injector 5 as a coating material 13, and after advancing an ejector half 1 and opening a mold clamp meal and a coating material 13 to homogeneity, it is made to leave and harden in the condition for 30 seconds. Then, ejection and the in mould coating injection-molded product 14 are obtained [a mold] for aperture mold goods.

[0047] Thus, the polypropylene resin constituent layer whose obtained in mould coating injection-molded products 14 are a coating layer and a base material is excellent in the adhesive property, and a cold energy cycle trial cannot exfoliate easily, either.

[0048] Although the case where the polypropylene resin constituent 8 is used as a raw material of mold goods is made into an example and drawing 1 explains, other raw materials can also be used instead of the polypropylene resin constituent 8. Moreover, in drawing 1, although illustrated, it can also form the ozone injector 4 and one coating-material injectors [two or more] 5 at a time. Moreover, the location to prepare can also be changed into the location of arbitration. The ozone injector 4 can also be made into the structure which serves as exhaust air, and can also discharge ozone content gas 12 from the ozone injector 4 in this case. Moreover, although ozone content gas 12 is discharged from the secondary space 11 by moving an ejector half 1 and closing metal mold in drawing 1, it can also discharge by air's permuting, where the secondary space 12 is held, or decompressing.

[0049]

[Example] The adhesive property of a coating layer and a polypropylene resin constituent layer was examined about the in mould coating injection-molded product obtained by the approach of examples 1 and 2 and example of comparison 1 drawing 1. In addition, the polypropylene resin constituent which contains the block polypropylene resin 90 weight section and the talc 10 weight section as a mold-goods raw material was used. The hardening mold acrylic resin coating which contains polyfunctional acrylic resin mixture and a peroxide as a coating material was used. A process condition and a result are shown in a table 1.

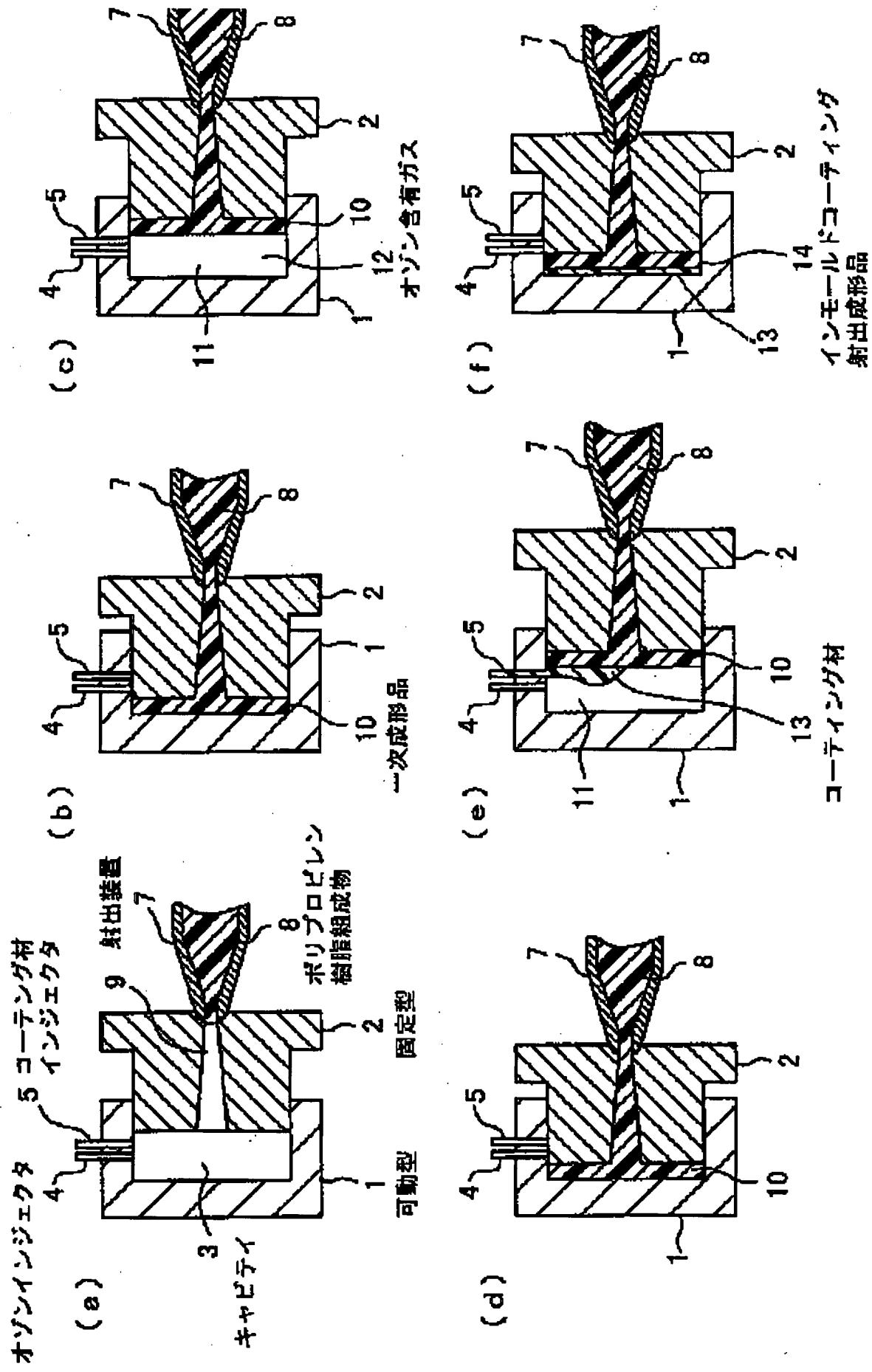
[0050]

[A table 1]
表1

	実施例 1	実施例 2	比較例 1
オゾン濃度 (g/m ³)	5	0.5	0
塗膜密着性 (個/個) * 1	100/100	66/100	0/100

*1 Paint film adhesion : slitting of every 11 every direction was put into the one-side square of 25mm on a painted surface, 100 grids were made, and adhesive tape was stuck on it. Adhesive tape was removed after that and the number of the grids which remained on the paint film side was counted.

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CLAIMS

[Claim(s)]

[Claim 1] In the manufacture approach of an in mould coating injection-molded product of coating the injection-molded product which uses polyolefin resin as the main raw material within metal mold, and manufacturing an in mould coating injection-molded product. The primary forming cycle which injects the raw material which uses as a principal component the polyolefin resin which carried out heating fusion to the cavity formed from a male and a female mold, and fabricates primary mold goods. The ozone contact process of making a male and a female mold estranging, forming space between metal mold and primary mold goods, supplying ozone content gas to this space, and making the front face of primary mold goods contacting. The manufacture approach of the in mould coating injection-molded product which includes the coating process which stiffens a coating material after pouring a coating material into the space formed between the exhaust gas process which discharges ozone content gas from metal mold, and metal mold and primary mold goods and coating primary mold goods.

[Claim 2] The manufacture approach according to claim 1 that polyolefin resin is polypropylene resin.

[Claim 3] The in mould coating injection-molded product manufactured from the manufacture approach according to claim 1 or 2.

[Translation done.]